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(54) Title of the Invention: **Adhesive Composition**

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SPECIFICATION**1. Title of the Invention**

Adhesive Composition

2. Claims

(1) An adhesive composition comprising (A) 15 to 80 % by weight of a thermoplastic copolymerized polyester elastomer whose acid components are (I) an aromatic dicarboxylic acid or ester forming derivative thereof in a ratio of 50 to 95 mol%, (II) a dimer acid, hydrogenation product thereof, or ester forming derivative thereof in a ratio of 5 to 40 mol%, and (III) an aliphatic dicarboxylic acid other than a dimer acid, or an ester forming derivative thereof in a ratio of 0 to 30 mol%; whose glycol components are (IV) an alkylene glycol with 2 to 10 carbon

atoms in a ratio of 60 to 97 mol% and (V) an aliphatic long-chain glycol with an average molecular weight of approximately 350 to 6000 in a ratio of 3 to 40 mol%, in which the sum of components (II) and (V) is 10 to 70 mol%, and whose limiting viscosity (measured at 20°C in a mixed solvent of phenol/tetrachloroethane = 1/1 (weight ratio)) is 0.5 to 1.5; and (B) 20 to 85 % by weight of an ethylene-vinyl acetate copolymer in which the vinyl acetate content is 10 to 50 % by weight.

3. Detailed Description of the Invention

(Field of Industrial Utilization)

The present invention relates to a hot melt adhesive composition which has a high adhesive strength and which is superior in terms of heat-resistant adhesive properties, and more specifically relates to a hot melt adhesive composition which is formed by mixing a specified polyester elastomer resin and ethylene-vinyl acetate copolymer at a specified ratio.

(Prior Art, and Problems to Be Solved by the Invention)

In recent years, hot melt adhesive agents have begun to be used in large quantities instead of conventional solution type adhesive agents or emulsion type adhesive agents because of the economy and convenience of such hot melt adhesive agents, e.g., lack of any need for a solvent, instantaneous bonding properties, adhesion to a relative broad range of adherends, etc.

Among these adhesive agents, the most widely used agents are ethylene-vinyl acetate copolymer type hot melt adhesive agents. Ethylene-vinyl acetate copolymers are used as mixtures with tackifying agents, plasticizers and the like. However, because such agents have poor heat-resistant adhesive properties and because the adhesive strength is not at a sufficiently high level, such agents cannot be used in product assembly or other fields requiring high-performance adhesive properties.

With the object of ameliorating such drawbacks, attempts have also been made to use polyester resins in blends with ethylene-vinyl acetate copolymers. For example, in Japanese Unexamined Patent Application No. 49-37941, an attempt is made to improve adhesive properties by mixing a polyethylene isophthalate or polyethylene isophthalate terephthalate and

an ethylene-vinyl acetate copolymer. Furthermore, in Japanese Unexamined Patent Application No. 51-115541, an attempt is made to improve adhesive properties with respect to metals by mixing an ethylene-vinyl acetate copolymer and a block polyester ether having a poly(tetramethylene oxide) glycol copolymerized as a soft segment. However, such polyester resins are inherently incompatible with ethylene-vinyl acetate copolymers, so that blending is performed in a phase-separated state; accordingly, the expected improvement in adhesive strength and improvement in heat-resistant adhesive properties cannot be obtained, so that practical use has not been achieved.

(Means Used to Solve the Above-Mentioned Problems)

The present inventors discovered that specified copolymerized polyesters containing dimer acids or hydrogenation products thereof and aliphatic long-chain glycols show superior compatibility with ethylene-vinyl acetate copolymers, and that an adhesive composition containing these compounds makes it possible to obtain a hot melt adhesive agent which eliminates the drawbacks described above, which has high adhesive strength and superior heat-resistant adhesive strength, and which is also superior in terms of weather resistance. This discovery led to the present invention.

Specifically, the present invention is an adhesive composition comprising (A) 15 to 80 % by weight of a thermoplastic copolymerized polyester elastomer whose acid components are (I) an aromatic dicarboxylic acid or ester forming derivative thereof in a ratio of 50 to 95 mol%, (II) a dimer acid, hydrogenation product thereof, or ester forming derivative thereof in a ratio of 5 to 40 mol%, and (III) an aliphatic dicarboxylic acid other than a dimer acid, or an ester forming derivative thereof in a ratio of 0 to 30 mol%; whose glycol components are (IV) an alkylene glycol with 2 to 10 carbon atoms in a ratio of 60 to 97 mol% and (V) an aliphatic long-chain glycol with an average molecular weight of approximately 350 to 6000 in a ratio of 3 to 40 mol%, in which the sum of components (II) and (V) is 10 to 70 mol%, and whose limiting viscosity (measured at 20°C in a mixed solvent of phenol/tetrachloroethane = 1/1 (weight ratio)) is 0.5 to 1.5; and (B) 20 to 85 % by weight of an ethylene-vinyl acetate copolymer in which the vinyl acetate content is 10 to 50 % by weight.

In the thermoplastic copolymerized polyester elastomer used in the present invention, hard segments consisting of an aromatic dicarboxylic acid component and soft segments consisting of an aliphatic long-chain glycol component are constructed in block form. The aromatic dicarboxylic acid component constituting the hard segments contributes to the heat-resistant adhesive properties by raising the softening point of the thermoplastic copolymerized polyester elastomer, and the amount used is in the range of 50 to 95 mol%, and preferably in the range of 60 to 90 mol%. If the ratio of the aromatic dicarboxylic acid component is less than 50 mol%, the heat-resistant adhesive properties and cohesive force are adversely affected. On the other hand, if this ratio exceeds 95 mol%, i.e., if the ratio of the dimer acid component is less than 5 mol%, the effect of the soft segments is reduced, so that plasticity disappears at low temperatures. The other aliphatic dicarboxylic acid component is appropriately used in the range of 0 to 30 mol% for the purpose of adjusting the softening point and melt viscosity of the resin. The dimer acid and aliphatic long-chain glycol component that constitute the soft segments contribute to an increase in the compatibility with the ethylene-vinyl acetate copolymer, and to a lowering of the glass transition temperature so that the plasticity at low temperatures is maintained. The amount of dimer acid is 5 to 40 mol% of the total acid component, and the aliphatic long-chain glycol component is 3 to 40 mol% of the total glycol component; furthermore, the sum of the amounts of both components is 10 to 70 mol%. If the sum of both components exceeds 70 mol%, the heat-resistant adhesive properties and cohesive force are adversely affected; on the other hand, if this sum is less than 10 mol%, the compatibility with the ethylene-vinyl acetate copolymer decreases, and the low-temperature characteristics deteriorate, so that the thermoplastic copolymerized polyester elastomer becomes hard and brittle. Thus, the presence of both a dimer acid and a long-chain glycol component is essential in the soft segments, and in cases where only a dimer acid is used alone, the compatibility with the ethylene-vinyl acetate copolymer is poor. Furthermore, since the dimer acid itself has a relatively low molecular weight, and since the compatibility of this component with the hard segment parts is good, the low-temperature characteristics are insufficient because of the fact that the two components are mixed together. Meanwhile, in cases where only an aliphatic long-chain glycol is used alone, the compatibility with the aromatic dicarboxylic acid is conversely poor, so that the heat-resistant adhesive properties and cohesive force are poor; moreover, the melt viscosity also increases. Specifically, in the thermoplastic copolymerized polyester elastomer,

the soft segments constructed from the aliphatic long-chain glycol are compatible with the ethylene-vinyl acetate copolymer, so that the blended state of both resins is improved, while the hard segments constructed with aromatic polyester segments as the chief component are not compatible with the ethylene-vinyl acetate copolymer, so that a drop in the softening point of the resin is suppressed, thus causing the composition in which both resins are mixed to have a superior adhesive strength and high heat-resistant adhesive strength.

Examples of aromatic dicarboxylic acids that may form constituent components of the thermoplastic copolymerized polyester elastomer of the present invention include terephthalic acid, isophthalic acid, phthalic acid, naphthalenedicarboxylic acid and the like. These acids may be used singly or in mixtures of two or more acids; in particular, terephthalic acid or a mixture of terephthalic acid and isophthalic acid is especially desirable for use. The dimer acid is a dimer of an unsaturated fatty acid with 10 or more carbon atoms; a desirable concrete example is a dimer of linolic acid. Empol 104 (manufactured by Emery, USA) may be cited as an example. Furthermore, Empol 1010 (manufactured by Emery, USA), in which the double bonds in a dimer of linolic acid are hydrogenated, is also desirable for use. For example, unsaturated dicarboxylic acids in which the methylene groups have 4 to 20 carbon atoms, such as succinic acid, adipic acid, azelaic acid, sebacic acid, dodecanedioic acid and the like, may be used singly or in mixtures of two or more acids as aliphatic dicarboxylic acids other than dimer acids.

A glycol with 2 to 10 carbon atoms is used as the aforementioned alkyl glycol; for example, ethylene glycol, trimethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol or pentyl glycol may be desirably used singly or in mixtures of two or more glycols. In regard to the components of the aliphatic long-chain glycols, polybutadiene glycols with an average molecular weight of approximately 350 to 6000, preferably approximately 600 to 4000, are desirable for use, such as 1,2-polybutadiene glycols, 1,4 polybutadiene glycols, copolymers thereof, mixtures or hydrogenation products thereof, polyisoprene glycols, hydrogenated polyisoprene glycols, polyolefin glycols and the like. In cases where poly(alkylene oxide) glycols, e.g., polyethylene glycols, polytetramethylene glycols and the like (which are generally widely used as long-chain glycol components) are used, the compatibility with the ethylene-vinyl acetate copolymer is poor, so that an adhesive composition with a superior thermal stability and weather resistance cannot be obtained. Furthermore, the adhesive strength also deteriorates. The

thermoplastic copolymerized polyester elastomer of the present invention has a limiting viscosity in the range of 0.5 to 1.5. In cases where the limiting viscosity is less than 0.5, a tendency is observed for the cohesive force to drop; on the other hand, if this viscosity exceeds 1.5, the melt viscosity becomes excessively high, so that the composition is unsuitable for use.

There are no particular restrictions on the method used to manufacture the thermoplastic copolymerized polyester elastomer of the present invention, and this manufacture can be accomplished by ordinary universally known methods. For example, a method can be used in which the aforementioned aromatic dicarboxylic acid component, dimer acid component, other aliphatic dicarboxylic acid components, alkylene glycol components and long-chain glycol component are directly esterified either simultaneously or in stages, or are subjected to an ester interchange reaction, after which polymerization is performed. Alternatively, a method can also be used in which a copolymer polyester with a high molecular weight or low molecular weight, a dimer acid or a hydrogenation product thereof, and the aforementioned long-chain glycol component are subjected to an ester interchange reaction, and in which polymerization is performed after this (depending on the case). Various types of universally known optional catalysts, stabilizers, modifying agents, additives and the like may be used in such polymerization or ester interchange reactions.

The ethylene-vinyl acetate copolymer used in the present invention has a vinyl acetate content of 10 to 50 % by weight. If the vinyl acetate content is less than 10 % by weight, the adhesive properties deteriorate, and the softness also disappears. On the other hand, if this content exceeds 50 % by weight, the adhesive agent becomes too soft, which is undesirable. The ethylene-vinyl acetate copolymer may also be partially converted into a ketone.

The mixture ratio of the thermoplastic copolymerized polyester elastomer (A) and ethylene-vinyl acetate copolymer (B) in the adhesive composition of the present invention is in the range of 15/85 to 80/20 (weight ratio), and is preferably in the range of 20/80 to 60/40. If the mixture ratio of component (A) is less than 15 % by weight, no effect in improving the heat-resistant adhesive properties is observed; on the other hand, if this ratio exceeds 80 % by weight, the adhesive strength deteriorates.

The adhesive composition of the present invention may also ordinarily contain resins that impart tackiness when mixed with an ethylene-vinyl acetate copolymer, as well as plasticizers, stabilizers, inorganic fillers and the like if necessary. In particular, resins that impart tackiness show poor compatibility with conventional polyester resins, so that in a composition consisting of an ethylene-vinyl acetate copolymer, a tackifying resin and a polyester resin, the dispersibility is poor, and a sufficient adhesive strength and heat-resistant adhesive properties cannot be obtained. However, the thermoplastic copolymerized polyester elastomer of the present invention is superior in terms of compatibility with tackifying resins, and the disperse state of the composition is extremely good, so that a superior adhesive strength is obtained.

A molten mixing method is desirable as the method used to mix the thermoplastic copolymerized polyester elastomer and ethylene-vinyl acetate copolymer in order to manufacture the adhesive composition of the present invention. For this purpose, kneading apparatuses such as ordinary rolls, kneaders, Banbury mixers, single- or twin-screw extruders or the like can be used.

The adhesive composition of the present invention can be applied in a molten state as a coating to the adherend by means of a common hot melt applicator, roll coater or the like; in addition, the adhesive composition of the present invention can be clamped between adherends after being formed into any of various configurations such as a powder form, chip form, tape form, cord form, film form, web form or the like, and the adherends can then be fused and bonded by heating the composition to a temperature above the softening point of the adhesive agent. Furthermore, the composition can be applied to a substrate as a coating agent, and used to modify the substrate surface. Moreover, the composition can be dissolved in a solvent, applied as a coating to a substrate and dried, and can then be used as a hot melt adhesive agent that is bonded by re-heating activation.

(Working Examples)

Below, the present invention will be described more concretely in terms of working examples. Furthermore, "parts" in the examples indicate "parts by weight".

Furthermore, characteristic values shown in the examples were measured by the following methods.

(1) Softening Point (°C)

The softening point was measured by the ring and sphere method according to JIS JA1-7.

(2) Softening Point in Shear Creep Test (°C)

A load of 300 g was applied in the shear direction to a test specimen (craft paper/craft paper) bonded over a bonding area of 2.5 cm × 2.5 cm, the temperature was elevated at the rate of 2°C/5 min, and the temperature at which the weight dropped was measured.

(3) Melt Viscosity (cps)

This property was measured at a temperature of 200°C by means of a Brookfield Thermo-Gel System HBTD (manufactured by Brookfield Engineering Laboratories, USA).

(4) Adhesive Peel Strength (kg/25 mm)

The adhesive peel strength was measured at a peeling rate of 50 mm/min at normal temperature (20°C) in accordance with JIS K-6854. The bonding conditions were as follows:

(a) Adherends: aluminum plate (2 mm thick)/aluminum plate (0.1 mm thick)

(b) Joining: the adhesive agent was melted by being heated to 200°C using a hot melt applicator, and was applied as a coating to bonded materials (width 25 mm, lap length .0 mm) and bonded by pressing.

(5) Weather Resistance

Evaluated using a sunshine weatherometer to determine the rate at which the tensile strength of the composition was retained following irradiation for 500 hours.

Working Examples 1 through 5 and Comparative Examples 1 and 2

0.01 mole of tetra-n-butyl titanate was added as a catalyst to 80 moles of dimethyl terephthalate, 20 moles of dimethyl isophthalate, 30 moles of a dimer acid (Empol 1010 manufactured by Emery, USA) and 200 moles of 1,4-butanediol, and an ester interchange reaction was performed by heating this mixture to 200°C for 1 hour in a nitrogen atmosphere.

Next, 15 moles of a hydrogenated polybutadiene glycol with a molecular weight of approximately 1000 (GI-1000 manufactured by Nippon Soda) and 0.02 moles of tetra- α -butyl titanate were added, and polycondensation was performed by heating in a vacuum for 4 hours at 240°C, thus producing a copolymerized polyester elastomer (I) (limiting viscosity 0.75, softening point 165°C, melt viscosity 260,000 cps).

This copolymerized polyester elastomer (I) and an ethylene-vinyl acetate copolymer (“EVAFLEX” EV-220 manufactured by Mitsui Polychemical, vinyl acetate content 28 % by weight, MI 150) were mixed in the proportions shown in Table 1, and the resulting mixtures were extruded from a twin-screw extruder with a screw diameter of 30 mm heated to a temperature of 200°C to produce adhesive compositions.

The adhesive compositions thus obtained showed a good mixed state, and the results obtained when the softening point, shear creep softening temperature, adhesive peel strength with respect to an aluminum plate and weather resistance were measured were as shown in Table 1.

Table 1 (CX = comparative example, WX = working example)

	Resin composition ratio (I)/EV-220	Softening point (°C)	Softening point in shear creep test (°C)	Adhesive peel strength (kg/25 mm)	Weather resistance, strength retention rate (%)
CX 1	90/10	160	150	3.0	60
WX 1	80/20	155	146	4.3	61
WX 2	50/50	149	133	5.3	58
WX 3	40/60	140	128	5.0	56
WX 4	30/70	122	110	4.2	60
WX 5	20/80	109	97	3.8	55
CX 2	10/90	94	81	2.5	57

Comparative Example 3

0.01 mole of tetra-n-butyl titanate was added as a catalyst to 70 moles of dimethyl terephthalate, 30 moles of dimethyl isophthalate and 160 moles of 1,4-butanediol, and an ester interchange reaction was performed by heating this mixture to 200°C for 1 hour in a nitrogen atmosphere.

Next, 30 moles of a polytetramethylene glycol with a molecular weight of approximately 1000 (PTMG-1000 manufactured by Mitsubishi Kasei) and 0.02 moles of tetra-n-butyl titanate were added, and polycondensation was performed by heating for 4 hours to 240°C in a vacuum, thus producing a copolymerized polyester elastomer (II) (limiting viscosity 0.83, softening point 158°C, melt viscosity 530,000 COS).

40 parts of this copolymerized polyester elastomer (II) and 60 parts of an ethylene-vinyl acetate copolymer ("EVAFLEX" EV-220 manufactured by Mitsui Polychemical) were extruded from a twin-screw extruder with a screw diameter of 30 mm heated to a temperature of 200°C to produce an adhesive composition.

The disperse state of this adhesive composition was not very good; the softening point was 128°C, the shear creep softening point was 83°C, and the adhesive peel strength with respect to an aluminum plate was 1.8 kg/25 mm. In regard to the weather resistance, deterioration was conspicuous in the case of irradiation for 200 hours, with the shape being broken down, and the strength retention rate was 0%. It should also be indicated that the weather resistance of the monomers of this copolymerized polyester (II) also showed a strength retention rate of 0% after 100 hours of irradiation.

Working Example 6

0.01 mole of tetra-n-butyl titanate was added as a catalyst to 60 moles of dimethyl terephthalate, 20 moles of dimethyl adipate, 20 moles of a dimer acid (Empol 1010 manufactured by Emery, USA) and 124.5 moles of 1,4-butanediol, and an ester interchange reaction was performed by heating this mixture to 200°C for 1 hour in a nitrogen atmosphere. Next, 10 moles of a liquid hydrogenated polybutadiene glycol with a molecular weight of approximately 1000 (GI-1000 manufactured by Nippon Soda) and 0.02 moles of tetra-n-butyl titanate were added, and polycondensation was performed by heating to a temperature of 230°C for 4 hours in a vacuum, thus producing a copolymerized polyester elastomer (III) (limiting viscosity 0.75, softening point 175°C, melt viscosity 410,000 cps).

30 parts of this copolymerized polyester elastomer (III), 40 parts of an ethylene-vinyl acetate copolymer ("EVAFLEX" EV-410 manufactured by Mitsui Polychemical, vinyl acetate

content 19 % by weight, MI 400), 15 parts of an esterification product of a hydrogenated rosin (Foral 85 manufactured by Hercules, USA) and 15 parts of a terpene phenol resin (YS Polystar T-115 manufactured by Yasuhara Chemical) were extruded from a twin-screw extruder with a screw diameter of 30 mm heated to 190°C to produce an adhesive composition. This adhesive composition showed a good disperse state, the softening point was 121°C, the softening point in the shear creep test was 109°C, and the adhesive peel strength with respect to an aluminum plate was 4.5 kg/25 mm.

(Effect of the Invention)

The adhesive composition of the present invention is superior to conventionally known ethylene-vinyl acetate type hot melt adhesive agents or hot melt adhesive agents consisting of ethylene-vinyl acetate copolymers and polyester resins in terms of adhesive strength and heat-resistant adhesive properties, and can be used in the bonding of metals, wood, paper, plastics, fibers and the like. Furthermore, the adhesive composition of the present invention also offers the advantage of being superior in terms of weather resistance.

Applicant: Unitika, Ltd.